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(71) Applicant (for all designated States except US): PERKINELMER INSTRUMENTS LLC [US/US]; 761 Main Avenue, Norwalk, CT 06859-0119 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: PROHASKA, Otto, J. [US/US]; 60 Brittania Drive, Danbury, CT 06811-2616 (US). LACONTI, Anthony, B. [US/US]; 7 Lovell Road, Lynnfield, MA 01940 (US). GINER, Jose, D. [US/US]; 103 Winchester Street, Brookline, MA 02446 (US). MANOUKIAN, Mourad [US/US]; 16 Edgecliff Road, Watertown, MA 02172 (US).

(74) Agents: WHITMYER, Wesley, W. Jr. et al.; St. Onge Steward Johnston & Reens LLC, 986 Bedford Street, Stamford, CT 06905-5619 (US).

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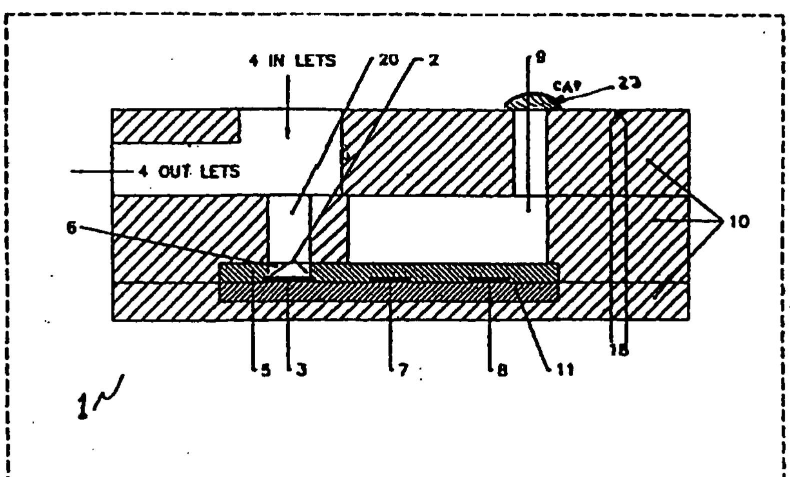
(54) Title: FILM TYPE SOLID POLYMER IONOMER SENSOR AND SENSOR CELL



THICK--FILM SENSOR CELL ASSEMBLY

(57) Abstract: A miniaturized gas sensor including film type electrodes, and a solid ionomer (5) electrolyte, for the detection of toxic gases, i.e., carbon monoxide, and other oxidizable or reducible gases and vapors is described. The all solid planar sensor cell has two or more film type electrodes arranged on a non conductive planar surface of a supportive material. The electrodes (3, 7, 8) are discrete and in intimate contact with the same solid polymer ionomer membrane. The sensor cell contains no liquid electrolyte and is operated in a potentiostatic or potentiodynamic mode. The unique feature of the sensor cell is that high sensitivity to a select gas or vapor is achieved by a novel three-phase contact area (2) design for a sensing electrode (3) which is easily accessible to the gas sample via small diffusion openings (6) or holes that penetrate through the solid polymer ionomer membrane layer above the sensing electrode. A significant signal to background noise enhancement is achieved for these film type sensor cells by processes that increase the three phase contact area.

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FILM TYPE SOLID POLYMER IONOMER SENSOR AND SENSOR CELL

FIELD OF THE INVENTION

The invention is in general directed toward a gas sensor and in particular to a miniaturized gas sensor with film type electrodes and a solid ionomer electrolyte.

BACKGROUND OF THE INVENTION

Film based techniques have been investigated for a wide variety of sensors, as reported by Wenyi et al., 1997; Hughes et al., 1997; Staley, 1996; Agbor et al., 1995; Tan and Tan, 1995; Menil et al., 1994; Kunnecke et al., 1994; Creasey and Varney, 1994; Geistlinger, 1993; Ishiji et al., 1993; Najafi et al., 1992; Hampp et al., 1992; Nakano and Ogawa, 1994; and Yamazoe and Miura, 1994. While solid-state gas sensors have the advantage of being able to operate at elevated temperatures, they also have the disadvantages of slow response and recovery time and a high internal operating temperature as reported by Liu et al., 1993; Narducci et al., 1993 and more recently by Schwebel et al., 1997; Sheng et al., 1997; and Micocci et al., 1997. Substantial development work needs to be done with this type of sensors before they can be utilized in battery-powered sensor instruments.

A Nafion®-coated metal oxide pH sensor was reported (Kinlen et al., 1994) with sputtered iridium oxide sensing and silver/silver chloride reference electrodes on alumina ceramic substrates. Nafion was used as a cation-selective ionomer coating in order to decrease the oxidation-reduction error generally affecting the performance of metal oxide pH electrodes. The use of Nafion as a polymer-electrolyte for a thin-film CO sensor was described (Yasuda et al., 1994) with macro-sized, sputtered Pt sensing electrodes and counter electrodes and a

smaller, sputtered Au electrode as a reference electrode. A 5 wt% n-propyl alcohol solution of Nafion (DuPont, 1100 EW) was used to form the polymer electrolyte film over the electrodes by casting. The polymer was washed and protonated in aqueous sulfuric acid prior to casting. The lifetime of this sensor was reported to be less than one month. During this one month lifetime the CO oxidation current decreased steadily down to a few percent of its original value without any period of stable measurement signal. The lifetime of the device may be extended by up to three years by lamination of the polymer electrolyte layer with a cast perfluorocycloether-polymer film in order to keep the CO permeability coefficient through Nafion constant. Theoretical calculations showed that the drift rate of the signal could be significantly reduced under these conditions.

Descriptions of typical state-of-the-art hydrated solid polymer electrolyte or ionomer sensors and sensor cells are provided by Kosek et al. U.S. Patent 5,527,446; LaConti and Griffith, U.S. Patent 4,820,386; Shen et al., U.S. Patent 5,573,648; and, Stetter and Pan, U.S. Patent 5,331,310. These sensor cells, based on hydrated solid polymer electrolyte or ionomer technology, have several advantages over conventional electrochemical sensor cells. The catalytic electrodes are bonded directly to both sides of a proton conducting solid polymer ionomer membrane providing a stable electrode to electrolyte interface. One side of the electrolyte membrane is flooded with distilled water, making the sensor cell self-humidifying and independent of external humidity. Since no corrosive acids or bases are used in the sensor cell, over 10 years lifetime has been demonstrated for solid polymer ionomer sensor cells. Finally, the sensor cells are easy to maintain, thus ideal for use in remote, unattended environments. Regular addition of water to the reservoir in the sensor housing every several months, and monthly calibration checks are the only requirements.

A disadvantage of the state-of-the-art sensors described above is that the signal-to-noise ratio may not be conducive to the detection of very low concentrations (parts per billion, ppb) of important environmental and biomedical

gases and vapors. Also, response time may be relatively slow, and reproducibility between sensors and sensor cells may be difficult to achieve. The sensors are also relatively costly.

SUMMARY OF THE INVENTION

The objective of this invention is to overcome the present limitations of miniaturized electrochemical sensors by uniquely interfacing advanced solid polymer ionomer membrane configurations with film type electrode structures to obtain low maintenance, highly sensitive, rapidly responsive, reproducible, sensor devices for environmental, industrial, and biomedical monitoring. By using a uniquely designed film type electrode array in intimate contact with an advanced solid polymer ionomer membrane film configuration, to form a three-phase contact area for the sensing electrode, where the gas sample, the electrode, and the solid ionomer can interface, a superior signal-to-noise ratio, rapid response time, and reproducibly of at least 1 to 10 ppb for a selected gas in an ambient environment can be achieved. Also, the projected cost of these sensors and sensor cells is very low since established film type solid-state manufacturing processes can be utilized.

The invention is also directed toward a treatment process for catalytically activating an ionomer membrane.

The invention is still further directed toward a gas sensor utilized in conjunction with a gas sensor control circuit.

The invention is also directed toward a gas sensor utilized in a gas sensing instrument.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a cross-sectional view of the film type planar sensor cell.

Figure 2a, shows a band-type film type sensing electrode.

Figure 2b, shows a flag-type film type sensing electrode.

Figure 2c shows a dot-type film type sensing electrode.

Figure 3 shows a block diagram of the complete film type gas or vapor sensing instrument.

Figure 4 shows a schematic of the gas sensor control circuits.

Figure 5 shows a calibration curve for ozone in air with band-type Au sensing electrode.

Figure 6 shows a calibration curve for SO_2 in air with band-type Pt sensing electrode.

Figure 7 shows a calibration curve for NO_2 in air with band-type Au sensing electrode.

Figure 8 shows a calibration curve for CO in air with band-type Pt sensing electrode.

Figure 9a and b show calibration curves for ozone in air with flag-type Au sensing electrode.

Figure 10 shows a calibration curve for NO in air with flag-type Au sensing electrode.

Figure 11 shows a calibration curve for CO in air with flag-type Pt sensing electrode.

DETAILED DESCRIPTION OF THE INVENTION

In **Figure 1**, the film type sensor cell assembly *(1)* includes a three-phase contact area *(2)* for the sensing electrode *(3)*, where the gas sample *(4)*, the sensing electrode *(3)*, and the solid ionomer membrane *(5)* can interface, as an essential part of the sensor design. The three-phase contact area *(2)* is formed by openings *(6)*, i.e., of circular shape, about 1.0 mm in diameter, in the solid ionomer

membrane *(5)* over the sensing electrode *(3)*. The sensor exhibits a fast response time because the solid ionomer membrane *(5)* layer acts simply as a proton conducting element between the film type sensing *(3)*, reference *(7)*, and counter *(8)* electrodes. Signal response is further enhanced by a special ionomer membrane treatment process which serves to "catalytically activate" the membrane. During this process platinum is imbedded in the solid ionomer membrane *(5)*. The improved response is due to the fact that the Pt, incorporated into the membrane *(5)*, contributes to the signal generation in the three-phase contact area *(2)*. The finely dispersed platinum is immobilized within and on the surface of the membrane *(5)* and does not affect the membrane's *(5)* ionic conductivity or water content. Also, this finely dispersed catalyst within the membrane *(5)* catalytically reacts with the permeating gases and prevents any reactive gases from reaching the reference electrode *(7)*, and disturbing it from its Pt/air (O_2) rest potential.

The film type sensor cell assembly shown in the schematic drawing of Figure 1 includes a water reservoir *(9)* to keep the solid ionomer membrane *(5)* hydrated. The water reservoir (9) is sealed with a cap (23). When using the devices in a humid atmosphere, a water reservoir *(9)* may not be required and would make the sensor housing design *(10)* significantly simpler, while the device could be packaged under humidified condition, ready for use.

Alternatively the openings in the ionomer membrane *(6)* can be slits or other suitable configurations for interfacing to form a three-phase contact area *(2)*. Also, in order to enhance the magnitude of the signal response and long-term stability, alternative materials such as Pt, gold, RuO_2 or other select metal or metal oxides can be deposited within the ionomer membrane *(5)* as finely dispersed particles.

Some select film type electrode configurations on non-conductive planar surfaces of a supporting material *(11)*, i.e., of alumina substrates, are showing practical sensing *(3)*, counter *(8)* and reference *(7)* electrode design in **Figure 2**.

A block diagram of the complete film type gas or vapor sensing instrument *(12)* is shown in **Figure 3**. A schematic of the gas sensor control circuits is shown in **Figure 4**. The sensor assembly *(1)* and its potential-control circuit *(13)* are integrated with a battery-operated microprocessor *(14)* of 32K memory, which samples the sensor signal as well as temperature and other signals at 10-, 20-, or 30-second intervals and stores an average value at intervals of 2, 5, or 10 minutes according to a programmable protocol. The data acquisition/storage unit in the microprocessor *(14)* can record 8 days of data, storing at 2-minute intervals, or up to 40 days storing at 10-minute intervals. In clinical testing to date, a 2-minute interval is suitable for one-day clinical studies and a 10-minute interval is appropriate for extended use. The microprocessor *(14)* with data acquisition/logic circuit can be programmed to sample more than one analog signal from the control circuit *(13)*, and to convert these to digital signals and store them (i.e., gas concentration and temperature) at preset intervals together with real-time data. Data are off-loaded to a personal computer by accessing the microprocessor *(14)* through an RS232 port. After downloading, the digital data are converted to engineering units of gas concentration and temperature, and can be graphed by a menu-driven Lotus® 123 spreadsheet. Through a potentiometer in the gain amplifier circuit *(15c)*, the device can be calibrated with calibrated gas samples, to indicate gas concentrations in the ambient. The potential-control circuit *(13)* shown in **Figure 3** is powered, in a preferred embodiment, by six, 1 ½ volt AA-size batteries *(16d)*. A typical microprocessor *(14)* with data acquisition-recording capability that has been successfully used is sold by ONSET Computers, Falmouth, MA, under the product name of "Tattletale Lite®." The sensor assembly *(1)* with its control circuit *(13)* is also designed to yield a current or voltage signal proportional to gas flux that could be used to continuously transmit the data to a remote receiving device or central monitoring station or unit.

The film type gas or vapor sensing instrument *(12)*, which is shown in **Figure 3**, includes the film type sensor cell assembly *(1)*, potential-control circuitry

(13), and the microprocessor *(14)* with the data acquisition-recording unit. The sensing instrument *(12)* is preferably battery operated, and has the ability to sample the gas or vapor and temperature signals at intervals and store in the random access memory (RAM) on the data acquisition board days to weeks of data. The data acquisition circuit microprocessor is programmed to sample and store the gas concentration signals at preset intervals. Data are off-loaded to a personal computer by accessing the microprocessor through an RS232 port.

The novelty of the measurement process is that it features potential (voltage) control as well as diffusion control through openings *(6)* in the membrane *(5)* of the sensor cell *(1)* for the sensitive and reproducible measurement of gas or vapor. The potential control circuit (13) (potentiostat) maintains the sensing electrode *(3)* at a fixed potential above the reference electrode *(7)* by passing current between the sensing *(3)* and counter electrode *(8)*. All three electrodes are located on the same surface of solid polymer ionomer *(5)*. A typical potentiostatic circuit for maintaining the sensing electrode *(3)* at a fixed potential versus a Pt/air (O_2) reference *(7)* is shown in **Figure 4**. The preferred potential range for the sensing electrode *(3)*, when detecting easily oxidizable gases such as CO, is 0 to 50 mV above the Pt/air (O_2) reference potential, 1.06 to 1.11 V above a Normal Hydrogen Electrode (N.H.E.). The useful potential-control range to avoid or minimize interference from air (O_2) is -300 to +300 mV versus the Pt/air (O_2) reference. In this potential range, the sensing electrode *(3)* has a highly active surface and gases or vapors are electrochemically oxidized or reduced very rapidly and completely; there is essentially zero concentration of gas or vapor at the sensing electrode *(3)* surface. The combined process of potential and diffusion control through openings in the membrane *(6)* creates a concentration gradient from the bulk gas sample to the sensing electrode *(3)* surface and results in a steady-state flux of gas or vapor and rapid electrochemical oxidation or reduction.

Referring to **Figure 4**, a block diagram of the sensor control circuit *(13)* is shown. The sensor control circuit *(13)* is designed to: 1) control the potential of the sensing electrode *(3)* at a predetermined voltage (the "potentiostatic voltage", or "E_{pot}"); 2) measure the temperature; 3) convert the gas concentration-related current to a temperature-compensated voltage signal; and 4) provide properly amplified voltage to the data acquisition/storage microprocessor *(14)*. An on-board micro power-regulated power supply *(16)* uses the microprocessor's *(14)* power supply to provide the required ±3.9 volts for the sensor circuitry. The DC power can be supplied by a 6-V battery *(16d)* or an AC adaptor *(16e)*.

The control amplifier portion *(17b)* of the sensor control circuit *(13)* consists of a micro power operational amplifier (e.g., MAX407 or LMC6062). The sensing *(3)*, counter *(8)* and reference *(7)* electrode portions of the sensor assembly *(1)* are in the feedback loop of the control amplifier *(17b)* as shown in **Figure 4**, a standard configuration for potentiostat circuits. An adjustable voltage divider *(17a)* allows the polarizing voltage (E_{pot}) to be set at a predetermined voltage range such as 0 to 50 mV. This signal is compared to the reference electrode *(7)* voltage (which appears with it at the summing junction) by the control amplifier *(17b)* of the sensor control circuit *(13)*. The latter adjusts the current through the sensor cell *(1)* to minimize the difference between the E_{pot} and the reference electrode *(7)* voltages.

The resulting sensor cell *(1)* current (flow of electrons from *(3)* to *(8)*), which is linearly related to the concentration of gas, is transformed into a voltage signal by the current-to-voltage converter *(15a)*. Temperature compensation of the sensor signal is effected in the next stage of amplification *(15b)* using a thermistor *(18a)* which is positioned in the gas sensor plastic housing *(10)*. The last stage of amplification *(15c)* provides the necessary inversion of the voltage signal as well as gain adjustment, to permit calibration for normal variations in sensitivity among sensors. The same type of micro power operational amplifier is used for these stages *(15a)*, *(15b)*, *(15c)* as for the control amplifier *(15b)*. The transformed

current signal is directed to an A/D channel on the data acquisition board of the microprocessor *(14)*.

Power for the sensor control circuit *(13)* is provided by a Duracell 6-V battery *(16d)* (PX 28A or 28L) through a micro power-regulated power supply *(16)*. The power supply *(16)* utilizes a voltage inverter (e.g., ICL 7660) *(16a)* to convert the positive battery voltage to a negative voltage of the same magnitude, and a positive voltage regulator (e.g., MAX663) *(16c)* and negative voltage regulator (e.g., MAX 664) *(16b)* to provide a stable ±3.9 volts.

Other embodiments may include protonic as well as anionic-hydroxide ion-exchange solid ionomer membrane film type configurations, containing the three phase contact area *(2)*, and can be used to detect important environmental and biomedical gases and vapors including CO, ozone, NO, NO_2, H_2S, SO_2, CO_2, hydrogen, hydrazine, ammonia, ethanol, and acetone. Other easily oxidizable or reducible gases such as Cl_2, HCl, formaldehyde, ethylene, or acetylene are readily detected at very low levels.

Figure 2-a, shows an embodiment comprising a band-type film type sensing electrode *(19)*, 0.5 x 4 mm^2 in size, between two 2 x 4 mm^2 rectangular counter electrode *(8)* structures. Two additional electrodes are included in the design, serving as reference electrodes *(7)*. The electrode closest to the sensing electrode *(19)* is used as Pt/air reference electrode *(7)*. The film type counter *(8)* and reference *(7)* electrodes are electroplated with Pt black to increase their actual surface area. When a Pt sensing electrode *(19)* is desired, it is also electroplated with Pt black to increase the measured current signal. A Nafion membrane, approximately 4.5 mil thick, is mechanically pressed onto the electrodes through a specially designed sensor housing *(10)*. A single opening *(6)* in the ionomer membrane *(5)*, approximately 1.0 mm in diameter provides gas access to the novel three-phase contact area *(2)*, where oxidation/reduction of the analyte occurs. The analyte stream is directed over the sensing electrode *(2)* at

moderately low flow rates. The analyte diffuses on to the sensing electrode *(2)* through a diffusion hole *(20)* in the sensor housing *(10)* and membrane *(5)* which has length-to-diameter ratios of approximately 3 or greater.

According to the present invention, band-type film type sensing electrodes *(19)* are used to measure most environmental gases, including ozone, SO_2, NO_2, and CO. Gold sensing electrodes are used when measuring ozone and NO_2 and Pt sensing electrodes are used when measuring SO_2 and CO. Calibration curves obtained with this design for ozone, SO_2, NO_2, and CO are shown in **Figures 5-8.**

Figure 2-b, shows an embodiment comprising a flag-type film type sensing electrode (21), 6 x 6 mm^2 surrounded by a U-shaped counter electrode (8); with a rectangular 1 x 4.5 mm^2 reference electrode *(7)* located below the sensing electrode*(21)*. Flag-type film type sensing electrodes *(21)* are used to measure ozone, NO and CO. Gold sensing electrodes are used to measure ozone and NO, while Pt electrode is used to measure CO. The film type counter *(8)* and reference *(7)* electrodes are electroplated with Pt black, as well as the sensing electrode*(21)*, when a Pt sensing electrode is desired. As in the embodiment in Figure 2-a, the solid ionomer electrolyte *(5)* is mechanically pressed onto the film type electrodes through a specially designed housing *(10)*. Six openings in the membrane *(6)*, approximately 1.0 mm dia. each, expose the three-phase contact areas *(2)* to the gas sample *(4)* under investigation. The film type sensor assembled in the specially designed housing *(10)* is placed in a 40-ml-volume diffusion chamber, to which the analyte is introduced, to simulate oxidation/reduction of the analyte under static flow conditions. The analyte *(4)* diffuses on to the sensing electrode *(21)* through six diffusion openings through the hardware *(20)* and membrane *(6)*, each opening having a total length-to-diameter ratio of approximately 3 or greater.

Calibration curves for ozone, NO and CO are shown in **Figures 9-11** respectively. It should be noted that the measured signal amplitude and low background noise levels obtained with a flag-type sensor *(21)* design is large

enough for the analytes *(4)* under investigation to be resolved in the single-digit ppb range. A specific advantage of the film type solid polymer ionomer membrane sensor in this invention is the high signal to background noise ratio.

The flag-type film type sensing electrode *(21)* design can be utilized to measure ethanol, methanol, acetone, hydrazine and hydrogen. Potentiostatic-controlled measurement results for the above mentioned gases are listed in **Table-1.**

Table 1

Gas/Vapor	Analyte Conc.	Solid Ionomer Electrolyte	SE	Signal
Ethanol:	1 mg/ml	Nafion	Pt	1.72 micro-amp
Methanol:	2 ml/60 ml	Nafion	Pt	180 nano-amp
Acetone:	300 micro-l/40 ml	Nafion	Pt	0.045 micro-amp
Hydrazine:	100 ppb	RAI	Au	9.3 nano-amp
Hydrazine:	100 ppb	Nafion	Au	3 nano-amp
Hydrogen:	2.5%	RAI	Au	120 nano-amp
Hydrogen:	2.5%	Nafion	Au	150 nano-amp
Hydrogen:	2.5%	RAI	Au	50 nano-amp
Hydrogen:	2.5%	Nafion	Au	97 nano-amp

Figure 2c shows an embodiment utilizing a dot-type film type sensing electrode *(22)* 2.3 mm in diameter, surrounded by four smaller dots of 1.2 mm dia. each. One of the lower smaller dots is used as a Pt/air reference electrode *(7)*, while the top two smaller dots are used as counter electrodes *(8)*. Counter *(8)* and reference *(7)* electrodes are electroplated with Pt black, and when a Pt sensing electrode is desired, it is also electroplated with Pt black. The ionomer membrane *(5)* is hot pressed onto the film type electrodes. One approximately 1.5 mm dia. opening *(6)* in the membrane *(5)* defines the three-phase contact area *(2)* for the

oxidation/reduction of the gas sample (analyte) *(4)* under investigation. The gas sample *(4)* stream is conducted over the sensing electrode *(22)* at moderately low flow rates.

Dot-type film type sensing electrodes *(22)* are used to measure NH_3 and H_2S. Potentiostatically controlled measurement results for the above mentioned gases are listed in **Table 2.**

Table 2

Gas/Vapor	Conc.	Solid Ionomer Electrolyte	SE	Signal
NH_3:	114 ppm	Neosepta	Pt	10 nano-amp
H_2S:	14 ppm	Nafion	Pt	700 nano-amp

Further embodiments of this invention include utilizing laser ablation methods for creating openings in the ionomer membrane in addition to the traditional methods of die punching. These openings may be of any appropriate shape. A diffusion barrier membrane may be placed over the openings to achieve permeation selectivity. Additionally, a filter material such as Purafil may be placed over, or in, the openings to remove interfering gasses or contaminants. Various heat or bonding methods may be employed for placing the ionomer film or membrane on the film type electrodes or the film type substrates.

The signal response of the three phase contact area can be enhanced through the use of a porous ionomer membrane film over the sensing electrode. Porosity can be achieved by utilizing a casting film of liquid ionomer that contains easily leachable fillers such as starch or polyglycols.

The sensing electrodes can be organized in multiple arrays or sets containing a necessary number of counter or reference electrodes. Reference electrodes such as Pt/air (O_2), PtO_2, or dynamic hydrogen electrode as described by Giner (1964) may be employed. Electrically driven 3- or 2-electrode film type configurations may be employed using potentiostatic, potentiodynamic or potential control. Two-electrode configurations require a reversible or stable counter-reference electrode such as Pt/air (O_2), PtO_2 or Pt/H_2 which has a higher BET (Brunauer, Emmett, Teller) surface area (25 m^2/g or larger) and/or larger geometric surface areas than the sensing electrode.

Electrochemically reversible electrodes may be used in 3 or 2 electrode configurations, but especially in a 2 electrode arrangement where the counter electrode also acts as a reference electrode. Electrochemically reversible electrodes are constructed of stable catalyst materials and usually have a relatively large electrochemical active surface area so that they remain stable and their potential is not perturbed by small current flow. Examples include PtO_2 and Ag/AgCl electrodes.

The sensor may be operated in a potentiodynamic mode of operation which serves to restore the original surface of the sensing electrode after gas or vapor sample adsorbs or perturbs the nature of the surface.

The sensor may also be used to detect other gases or vapors that are easily oxidizable or reducible, such as aldehydes (formaldehyde, acetaldehyde), Cl_2, HCl, ethylene, acetylene.

CLAIMS

1. A sensor cell for detecting gases comprising: a substrate; a surface; a solid, ionomer membrane in intimate contact with said substrate and surface; a sensing electrode; a counter electrode; and a reference electrode, said sensing, counter and reference electrodes in intimate contact with said surface; and an open three-phase area in said membrane, proximate to said sensing electrode, said area providing contact among said gases to be detected, said sensing electrode, and said membrane.

2. The apparatus of claim 1 further comprising openings in said membrane proximate to said sensing electrode which facilitate contact in said open three-phase area.

3. The apparatus of claim 2 wherein said openings in said membrane contain a particulate catalyst which electrically contacts said sensing electrode.

4. The apparatus of claim 1 wherein said sensing, counter and reference electrodes are in close contact with said membrane.

5. The apparatus in claim 1 whereby said membrane is a proton exchange membrane.

6. The apparatus in claim 1 whereby said membrane is an anion, hydroxide ion exchange membrane.

7. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes are formed by deposition on said membrane.

8. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes are formed by deposition on said substrate.

9. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes are metallic.

10. The apparatus of claim 1 wherein said sensing, counter, and reference electrodes comprise a material selected from the group consisting of Pt,Au, C, platinized Pt, and platinized Au.

11. The apparatus of claim 1 wherein said electrodes are coated with a thin proton exchange film layer which acts to increase the threephase area.

12. The apparatus of claim 1 where said solid ionomer membraneis comprised of dispersed metallic particles which act to increase the threephase contact area and to enhance signal response and stability.

13. The apparatus of claim 1 wherein said membrane, substrate, and surface are brought into intimate contact by bonding techniques.

14. The apparatus of claim 1 wherein said ionomer membrane is humidified by aqueous material.

15. The apparatus of claim 1 wherein said sensor cell is electronically controlled in a 2 electrode sensor configuration.

16. The apparatus of claim 1 wherein said sensor cell is electronically controlled in a 3 electrode sensor configuration.

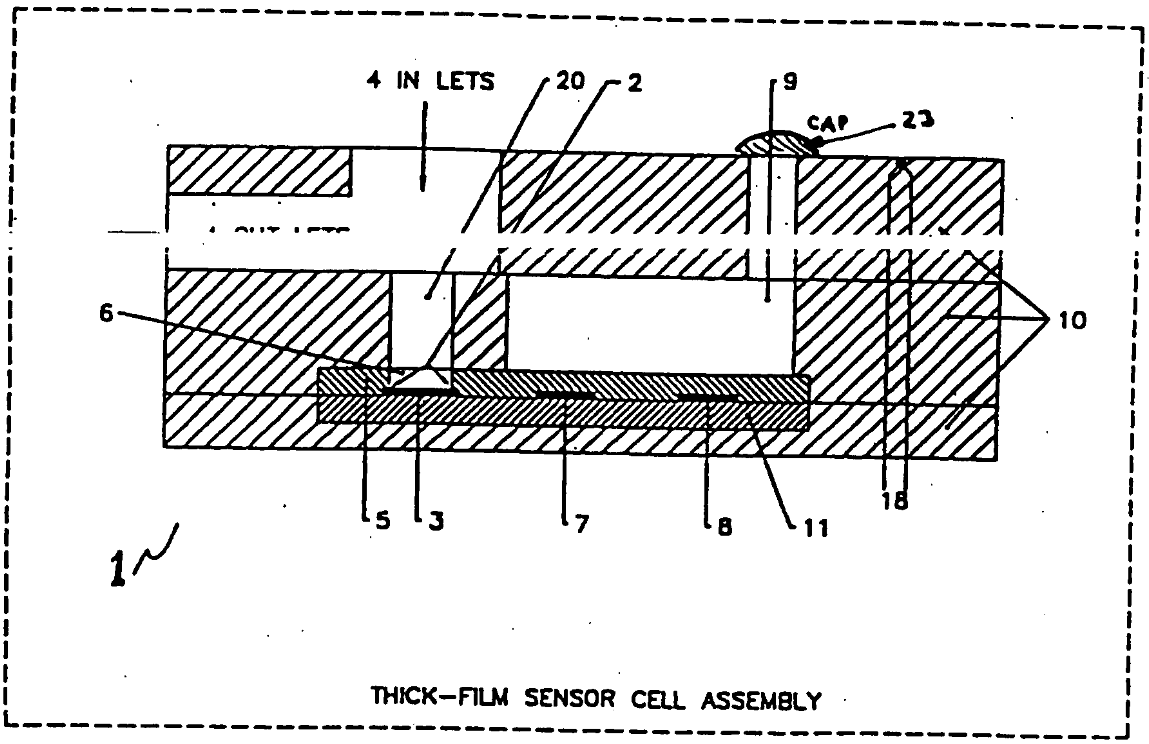
17. The apparatus of claim 1 wherein said sensor cell is electronically controlled by a potentiostatic circuit connected to said sensing, counter and eference electrodes.

18. The apparatus of claim 1 wherein said sensor cell is electronically controlled by a potentiodynamic circuit connected to said sensing, counter and reference electrodes.

19. The apparatus of claim 1 wherein said sensor cell is dectronically controlled by a constant voltage source connected to said sensing electrode and an electrochemically reversible counter electrode acting as a reference electrode.

20. The apparatus of claim 1 further comprising a microprocessor for real time data readout, data storage and retrieval, and remote data transmission.

21. The apparatus of claim 1 incorporated into a gas sensing instrument.


4 IN LETS
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THICK-FILM SENSOR CELL ASSEMBLY

Figure 1

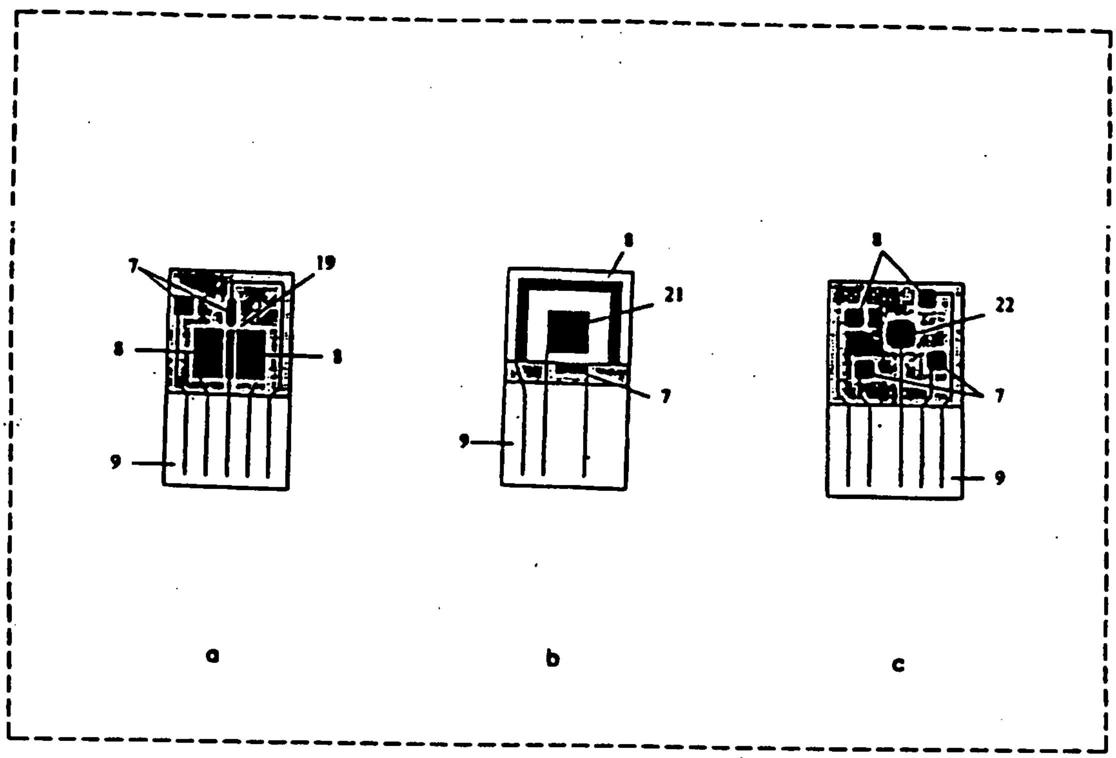

Figure 2

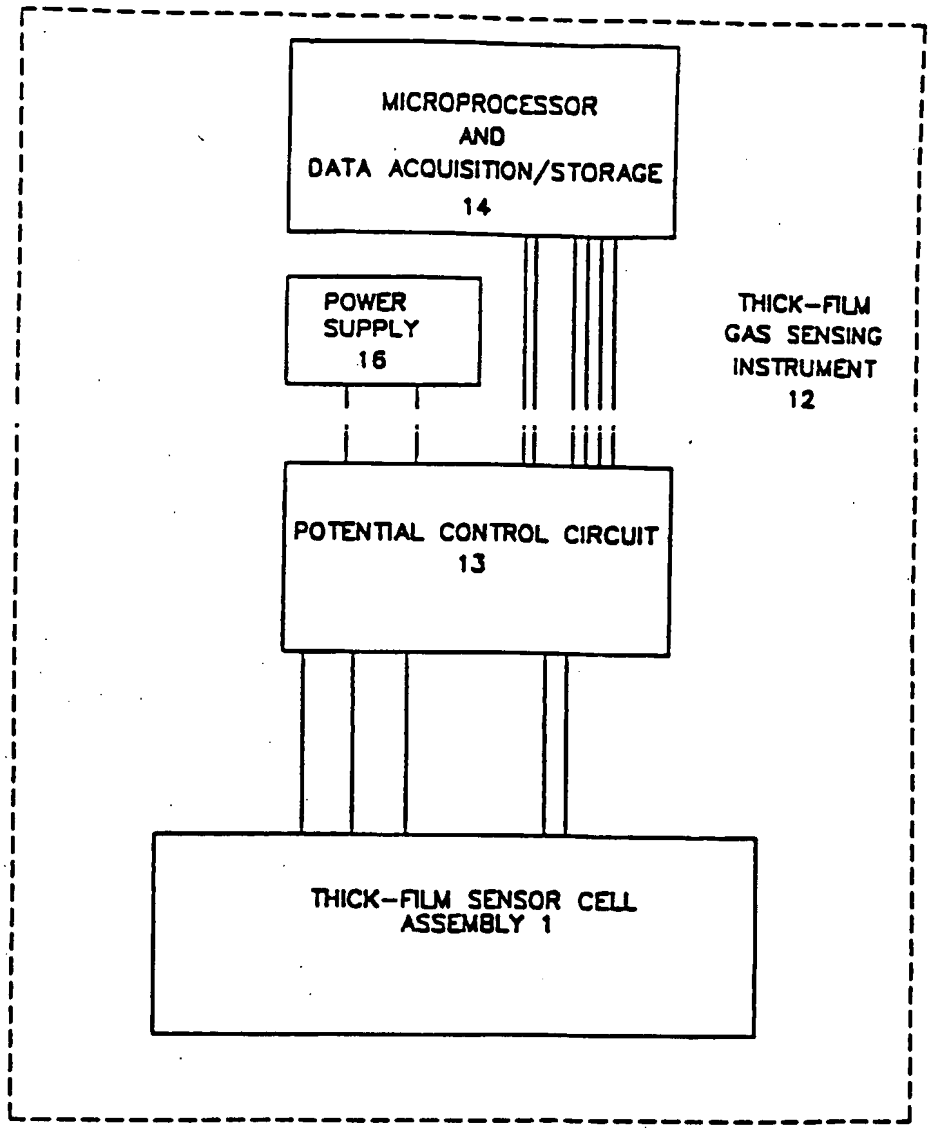
MICROPROCESSOR
AND
DATA ACQUISITION/STORAGE
14
POWER
SUPPLY
16
THICK-FILM
GAS SENSING
INSTRUMENT
12
POTENTIAL CONTROL CIRCUIT
13
THICK-FILM SENSOR CELL
ASSEMBLY 1

Figure 3

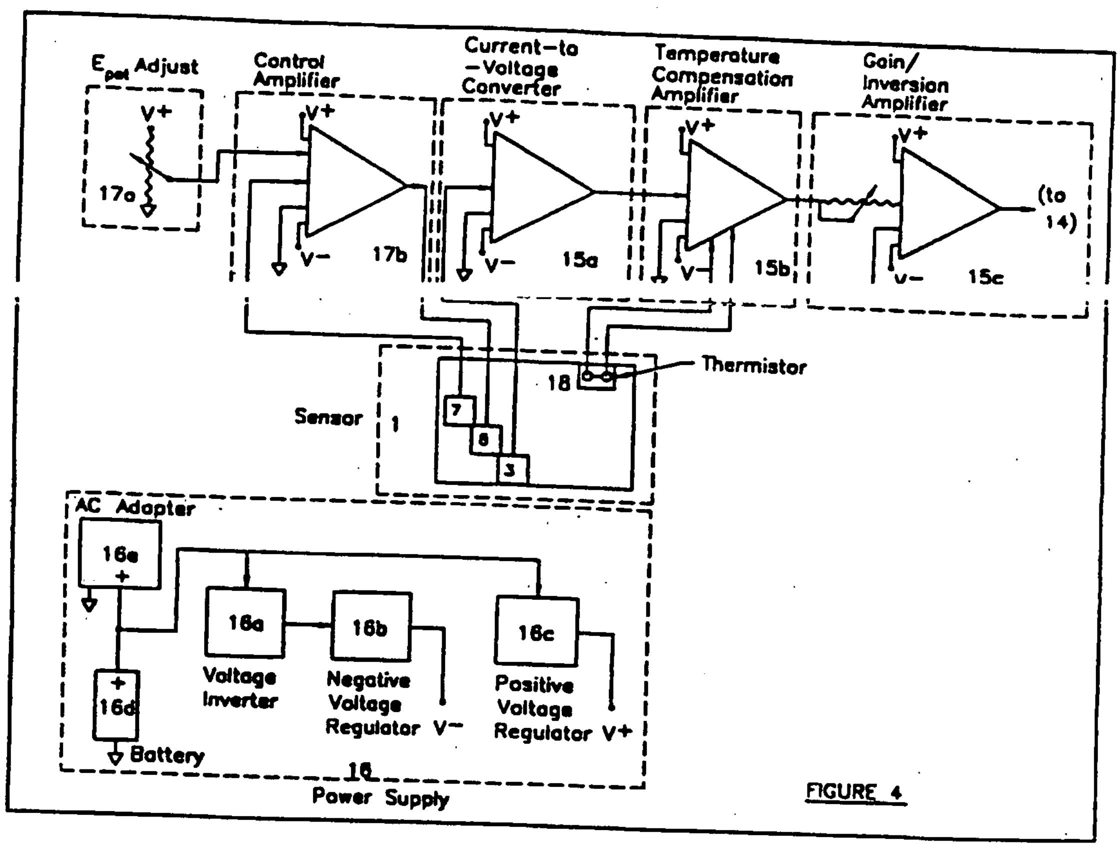
E$_{pot}$ Adjust
Control Amplifier
Current-to-Voltage Converter
Temperature Compensation Amplifier
Gain/ Inversion Amplifier
V+
V−
17a
17b
15a
15b
15c
(to 14)
Thermistor
18
Sensor
1
7
8
3
AC Adapter
16e
16a
16b
16c
16d
Voltage Inverter
Negative Voltage Regulator
Positive Voltage Regulator
Battery
16
Power Supply
FIGURE 4

Figure 4

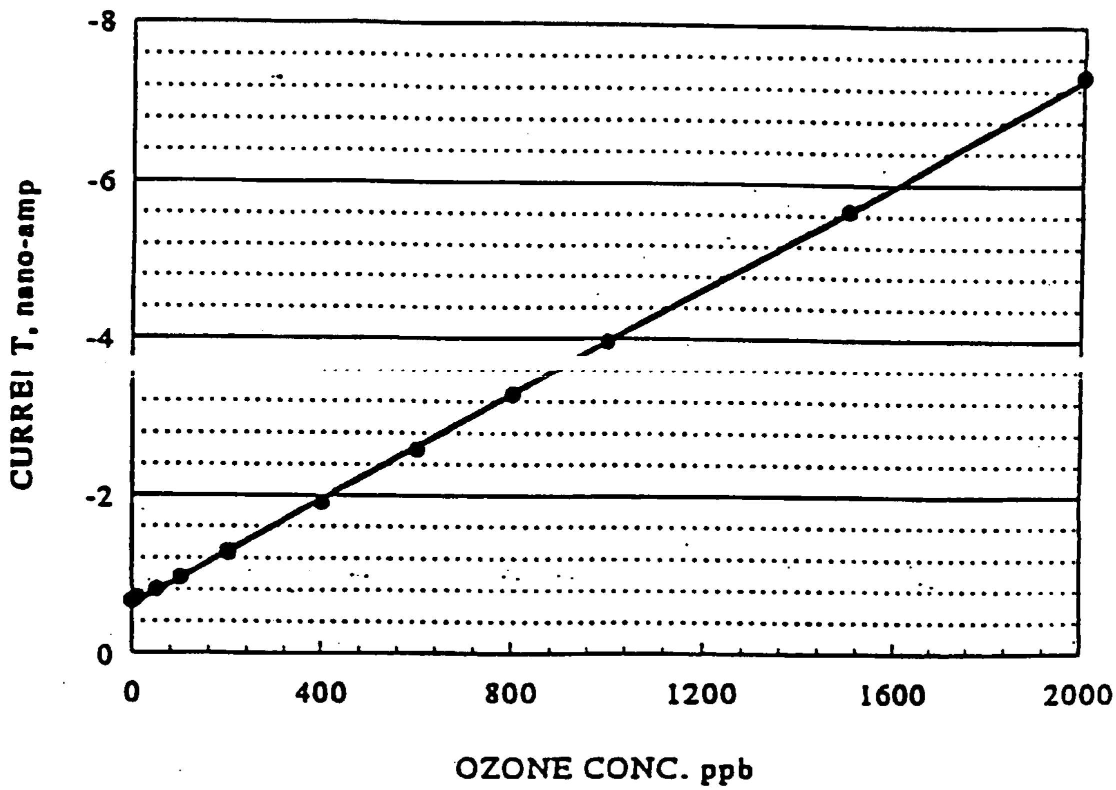
-8
-6
-4
-2
0
CURREI T, nano-amp
0
400
800
1200
1600
2000
OZONE CONC. ppb

Figure 5

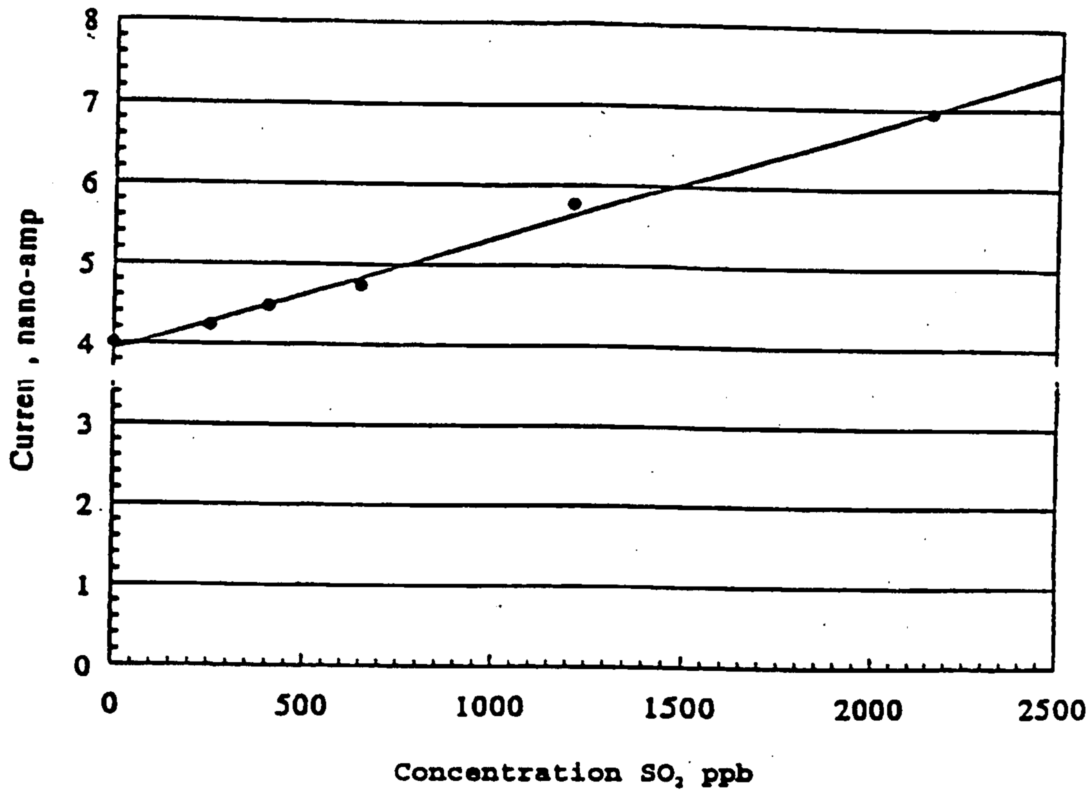
Curren , nano-amp
8
7
6
5
4
3
2
1
0
0
500
1000
1500
2000
2500
Concentration SO_2 ppb

Figure 6

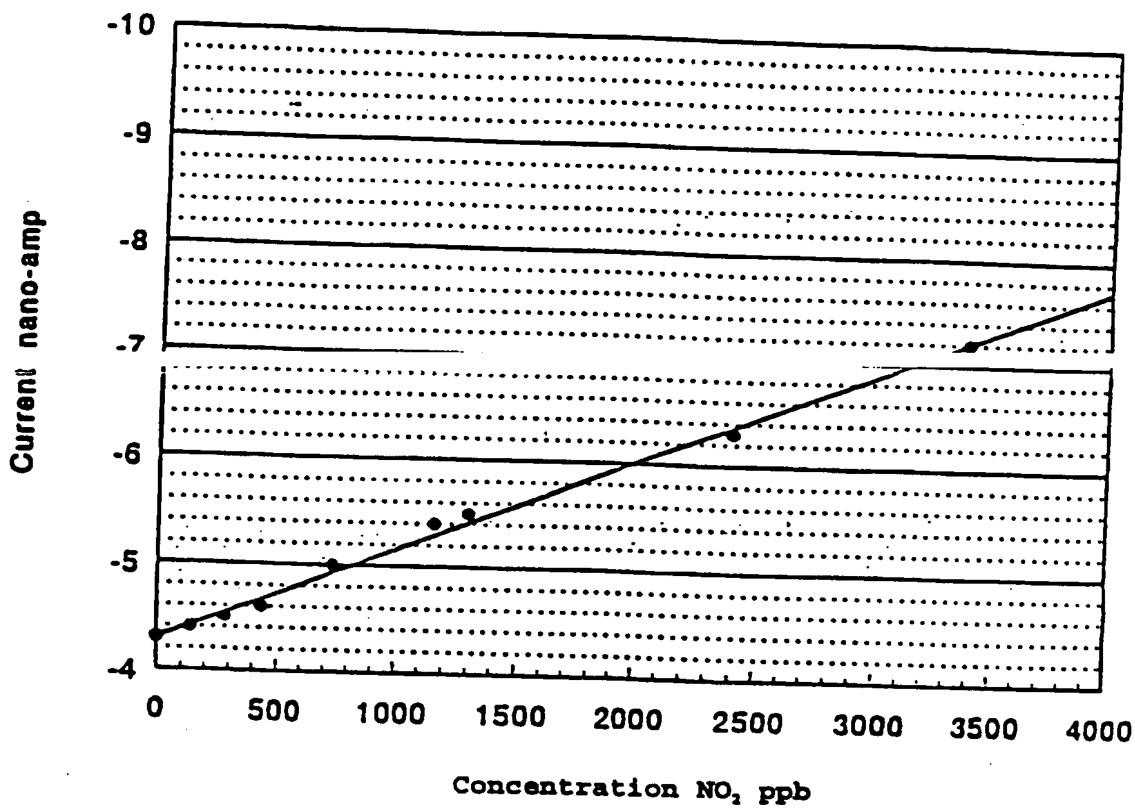
-10
-9
-8
-7
-6
-5
-4
Current nano-amp
0
500
1000
1500
2000
2500
3000
3500
4000
Concentration NO_2 ppb

Figure 7

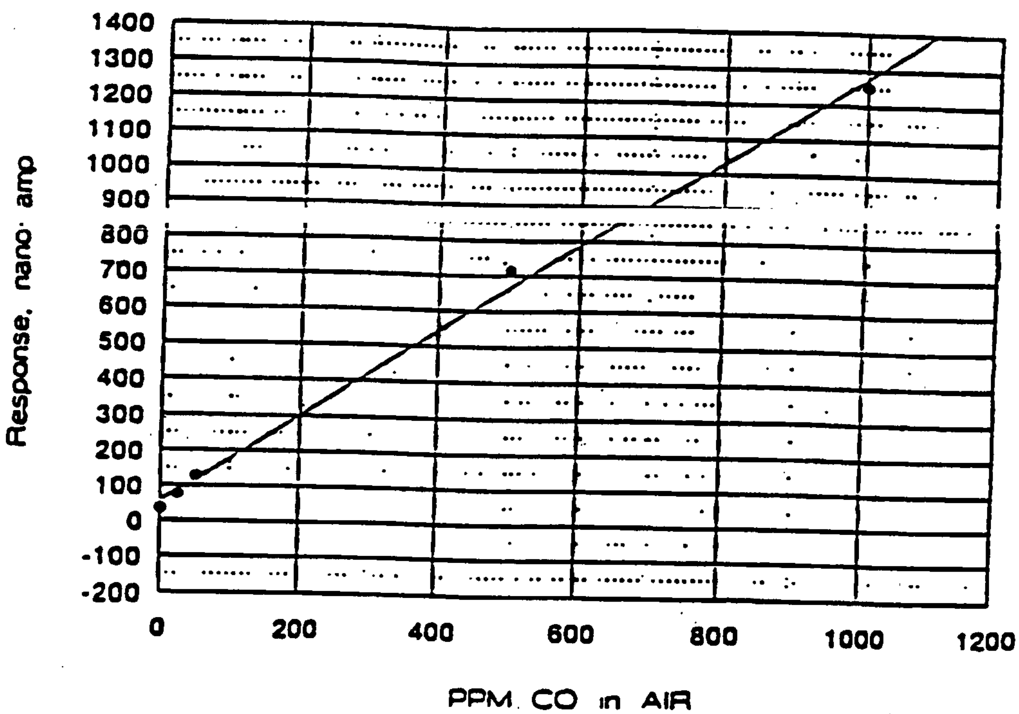
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
Response, nano amp
0
200
400
600
800
1000
1200
PPM CO in AIR

Figure 8

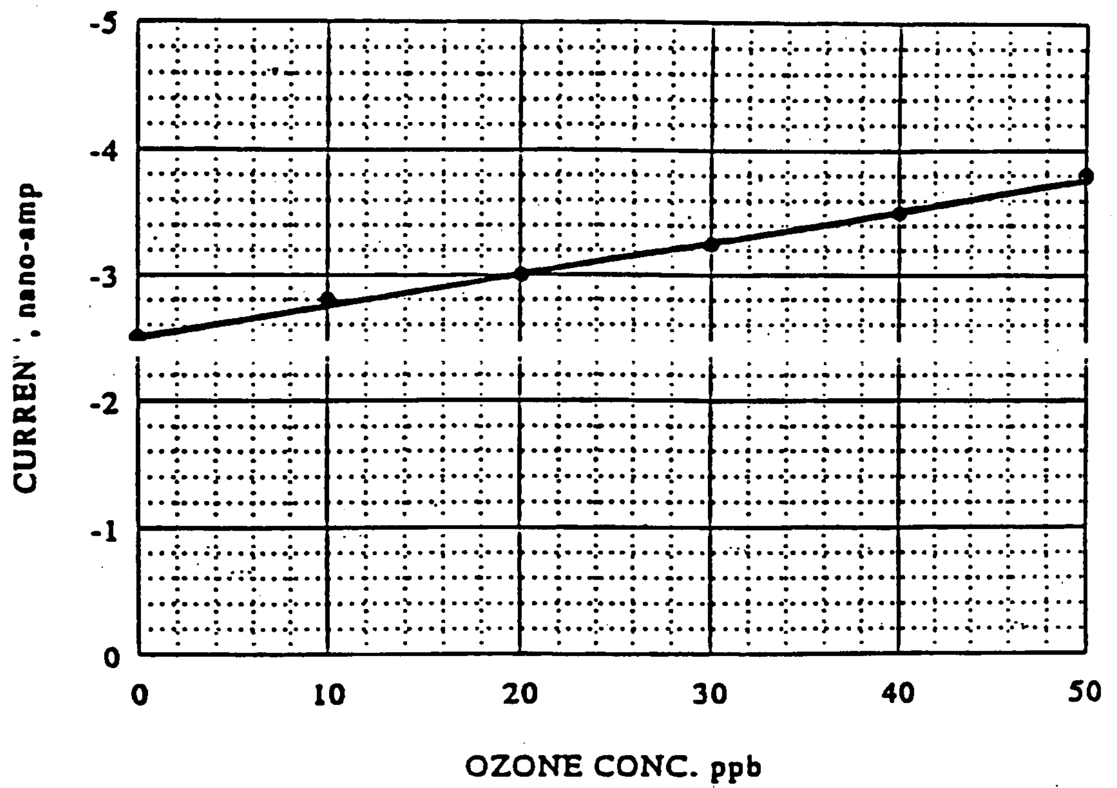

Figure 9a

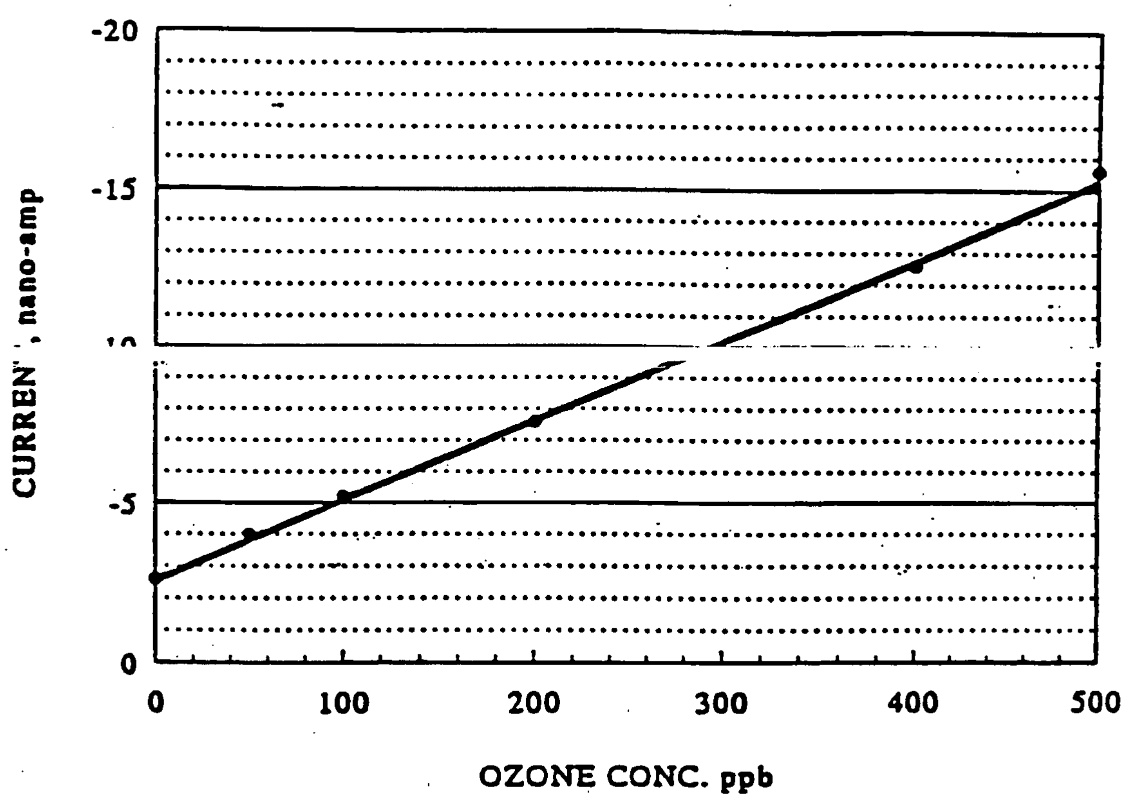
-20
-15
-10
-5
0
CURRENT, nano-amp
0
100
200
300
400
500
OZONE CONC. ppb

Figure 9b

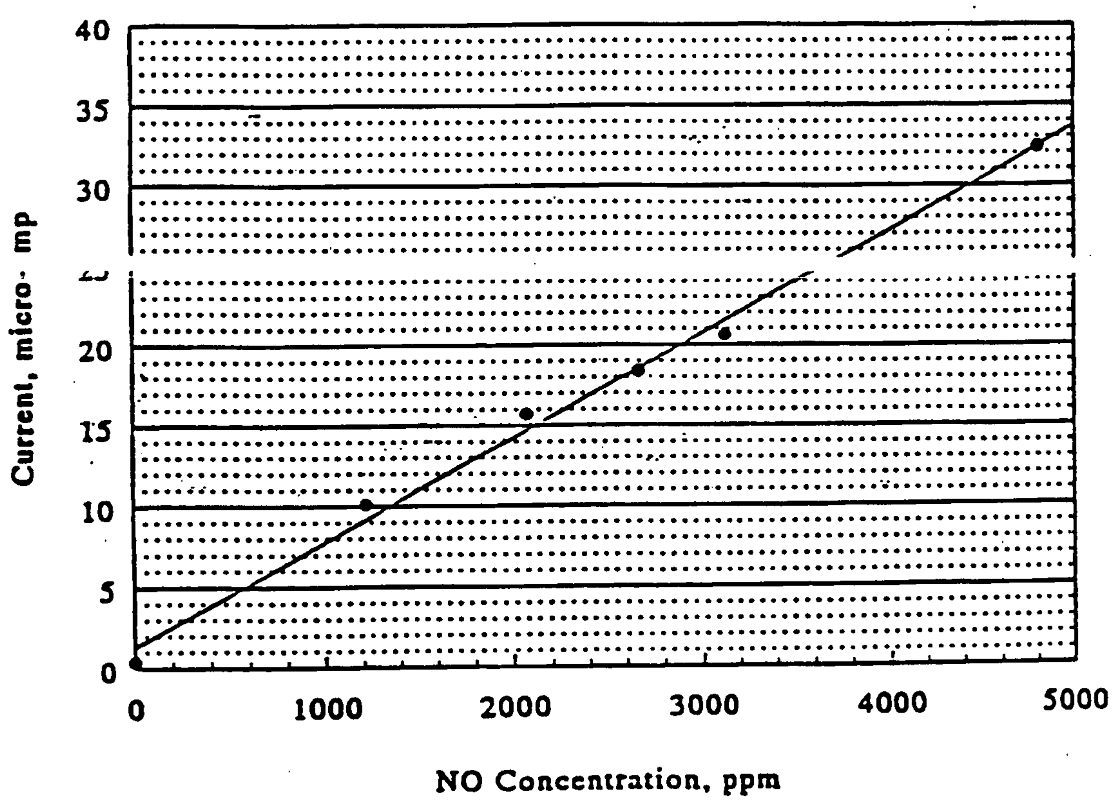
40
35
30
20
15
10
5
0
Current, micro- mp
0
1000
2000
3000
4000
5000
NO Concentration, ppm

Figure 10

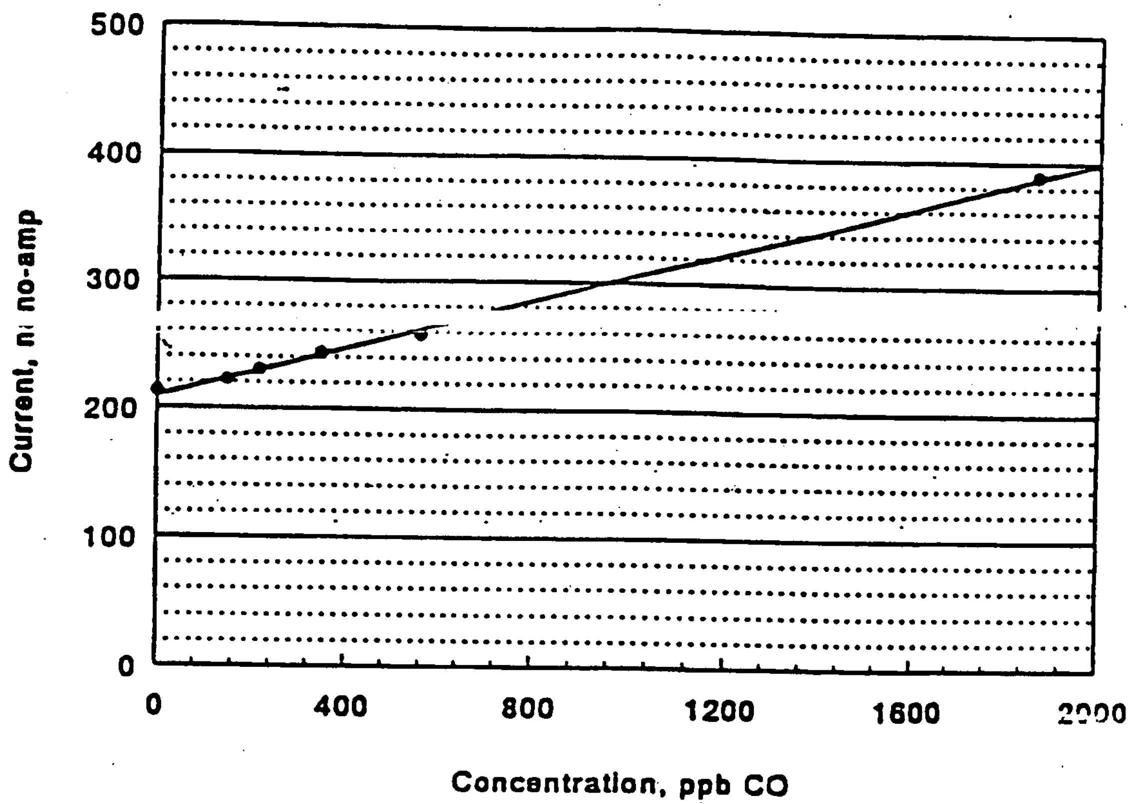
500
400
300
200
100
0
Current, n no-amp
0
400
800
1200
1600
2000
Concentration, ppb CO

Figure 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/31795

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :G01N 27/407
US CL :204/426
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/406, 412, 415, 421-429, 431, 432

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,172,770 A (SEMERSKY ET AL) 30 October 1979, see column 4, lines 40-54.	15, 19
A	US 4,812,221 A (MADOU ET AL) 14 March 1989, see column 2, line 50 to column 5, line 54.	1-21
Y	US 4,820,386 A (LACONTI ET AL) 11 April 1989, see column 4, lines 27-34.	7
Y	US 4,851,104 A (CONNERY ET AL) 25 July 1989, see column 2, line 36.	20
X --- Y	US 4,900,405 A (OTAGAWA ET AL) 13 February 1990, see columns 5, line 17 to column 14, line 48.	1-14, 16- 18, 21 --- 15, 19, 20

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
05 FEBRUARY 2001	03 APR 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
[signature]
T. TUNG
Telephone No. (703) 308-3329

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/31795

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,527,446 A (KOSEK ET AL) 18 June 1996, see column 5, line 5.	6